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ORIGINAL PAPER

Magnetocaloric Effect Near Room Temperature of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06, 0.07, 0.08$) Manganites

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Abstract Structural and magnetic properties of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08) manganites synthesized using the solid-state reaction method were investigated. Rietveld refinement of the X-ray diffraction patterns shows that all our samples crystallize in the orthorhombic structure with *Pbnm* space group. The temperature dependence of magnetization reveals that all the samples exhibit a ferromagnetic (FM) to paramagnetic (PM) transition at temperatures of 279 K for $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$, 286 K for $La_{0.67}Ca_{0.26}Sr_{0.07}MnO_3$, and 293 K for $La_{0.67}Ca_{0.25}Sr_{0.08}MnO_3$. Using Arrot plots, the phase transition from FM to PM is found to be of second order. The maximum of the magnetic entropy change ($-\Delta S_M$) is found to be 3.37, 2.74, and 2.60 J kg^{-1} K^{-1} for $x = 0.06$, 0.07, and 0.08 under a magnetic field change of 3 T. The relative cooling power (RCP-1) for $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ sample is 152, 162, and 164 J kg^{-1} for $x = 0.06$, 0.07, and 0.08. According to these results, these kinds of samples are promising materials for magnetic refrigerants in the room-temperature region.

Keywords Manganite · Magnetocaloric effect · Magnetic entropy change · Relative cooling power

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1 Introduction

Over the past few years, the manganites with the formula $Ln_{1-x}A_xMnO_3$ (Ln = trivalent rare earth, A = divalent alkaline earth) have attracted much attention due to their extraordinary magnetic and electronic properties and their promise for future technological applications [1]. In particular, the $La_{1-x}Sr_xMnO_3$ compounds are given particular attention because of their interesting magnetic properties such as colossal magnetoresistance (CMR) and magnetocaloric effect (MCE) [2]. Guo and colleagues [3] measured the large magnetic entropy change in perovskite-type manganese oxides and found that the compound $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33) showed larger magnetic entropy change than that of Gd.

Moreover, it has been reported that the magnetocaloric parameters in a series of manganite compounds belonging to the family $La_{0.67}Ca_{0.33-x}Sr_xMn_{3+\delta}$ with $x \in [0; 0.33]$, and it was found that the Curie temperature can be tailored between 267 and 369 K by the substitution. Also, it was found that the maximum magnetic entropy change of this compound, prepared by the technique of the glycine-nitrate synthesis with composition corresponding to $x = 0.055$, had the closest value of Curie temperature to that of the

gadolinium [4]. In this context, the study of MCE in such lanthanum manganese compounds can be still of great interest. In this work, substitutions of $x = 0.06$, 0.07, and 0.08 are analyzed.

2 Experimental

Stoichiometric samples of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08) were prepared by the conventional solid-state reaction using purity commercial powders La_2O_3, $MnCO_3$, $SrCO_3$, and $CaCO_3$ (99 %) as precursors. The precursors were ball-milled in ethanol for 1.5 h. The ball-milled slurry was filtered and dried at 60 °C for 3 h. The as-dried powders were ground and presintered at 1100 °C and sintered at 1150 °C for 8 h with intermediate grinding. The heating temperature and cooling rates for all the samples was 17 °C/min. The X-ray diffraction (XRD) patterns were recorded on a RIGAKU DMAX-2200 diffractometer equipped with a Cu-Kα anode ($\lambda = 1.54056$ Å) in the 20° −80° 2θ range with a step size of 0.02°. Rietveld refinement analysis of the structure was performed using the MAUD program [5]. Magnetization measurements versus temperature in the range of 234–344 K versus an applied magnetic field up to 3 T were carried out using a vibrating sample magnetometer (VSM).

3 Results and Discussion

3.1 Structural Characterization

Figure 1 shows the indexed XRD patterns of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08). The XRD patterns reveal that all solid solutions are a single phase corresponding to the orthorhombic perovskite structure with space group *Pbnm*. Refined cell parameters and the X-ray density are summarized in Table 1.

Table 1 Refined structural parameters of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08)

	$x = 0.06$	$x = 0.07$	$x = 0.08$
a (Å)	5.474(1)	5.455(1)	5.451(1)
b (Å)	5.480(1)	5.494(1)	5.494(1)
c (Å)	7.735(1)	7.762(1)	7.765(1)
ρ (g/cm^3)	6.067(1)	6.069(1)	6.083(1)

3.2 Magnetic Characterization

In order to determine the Curie temperature of all samples, their temperature dependence of magnetization, $M(T)$, was measured under an applied magnetic field of 0.01 T (Fig. 2). All the samples showed a single magnetic transition from ferromagnetic (FM) to paramagnetic (PM) as the temperature increases. The FM-PM transition temperature or Curie temperature (T_c) is defined at the inflection point of $M(T)$ curves. The T_c was found to be 279, 286, and 293 K for $x = 0.06$, 0.07, and 0.08, respectively. These temperatures are displaced with respect to the value of 267 K of the parent compound $La_{0.67}Ca_{0.33}MnO_3$ [6].

In order to calculate the change of magnetic entropy of the compounds, magnetization curves versus the applied magnetic field, from 0 to 3 T, at different temperatures, were measured in the range from 239 to 334 K with a step of 5 K (Fig. 3). Below T_c of every sample, the magnetization increases sharply for values of applied field lower than 0.5 T, and it tends to saturation for higher magnetic fields. Above T_c, the magnetization M increases more smoothly, as a typical behavior of paramagnetic materials. This decrease is mainly due to the thermal agitation which tends to disorder the magnetic moments. This variation indicates that

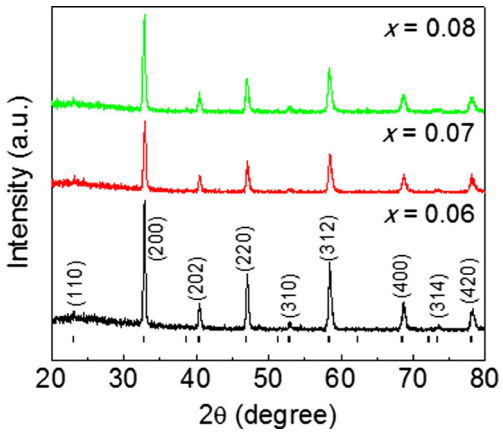

Fig. 1 X-ray diffraction (XRD) patterns at room temperature for $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08) samples. The *vertical bars* indicate the expected reflection positions

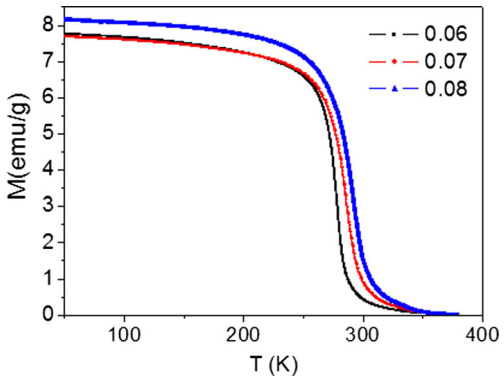

Fig. 2 Temperature dependence of magnetization in a constant magnetic field of 0.01 T ($x = 0.06$, 0.07, and 0.08)

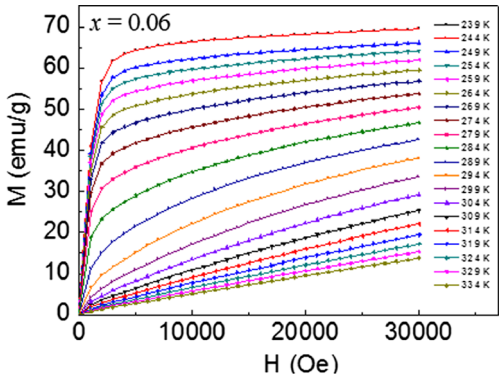

Fig. 3 The isothermal magnetization curves for the sample $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$. The *error bars* are smaller than data points

there is a large magnetic entropy change associated with the FM-PM transition temperature occurring at T_c [7].

The nature of the magnetic transition in the samples was checked using the Banerjee criterion [8]. According to this criterion, the slope of H/M versus M^2 curves denotes whether the observed magnetic transition is of the first order (negative slope) or second order (positive slope). H/M versus M^2 curves obtained for all $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$, 0.07, 0.08) samples clearly indicate positive slope in their complete M^2 range, and this confirms the transition to be of the second order. A typical set H/M versus M^2 curves for the $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06$) sample is shown in Fig. 4.

Using these data, the magnetic entropy change (ΔS_M) versus temperature for a material that undergoes a second-order transition was determined from the discrete form of the following equation [8]:

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{1}$$

Experimentally, two different methods are often used to evaluate the magnetic entropy change, ΔS_M. The first one is

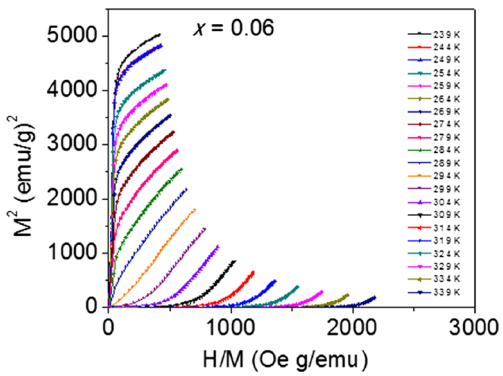

Fig. 4 Arrot plot (H/M versus M^2) of $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$ at different temperatures. The *error bars* are smaller than data points

the measurements of the MT curve under different applied magnetic fields. The second one is the measurement of the curve under different temperatures [9]. In this work, we used the second method to calculate the magnetic entropy change.

In the case of isothermal magnetization measurement with small discrete field and temperatures intervals, ΔS_M can be approximated as follows [10]:

$$|\Delta S_M| = \sum \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i \tag{2}$$

where M_i and M_{i+1} are the experimental data of the magnetization at T_i and T_{i+1}, respectively, and the ΔH is the difference of the applied magnetic field.

The magnetic entropy change (ΔS_M) as a function of temperature for the $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ sample investigated at a maximum magnetic field of 3 T is shown in Fig. 5. The magnetic entropy change reaches the maximum value around T_c, and it increases with decreasing x. It can be seen that the magnetic entropy change depends on x for this samples. The maximum value of magnetic entropy change decreases from 3.37 J kg^{-1} K^{-1} for $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$, 2.74 J kg^{-1} K^{-1} for $La_{0.67}Ca_{0.26}Sr_{0.07}MnO_3$, and 2.60 J kg^{-1} K^{-1} for $La_{0.67}Ca_{0.25}Sr_{0.08}MnO_3$ samples. Comparing ΔS_M values of these compounds with those of more complex manganite system and with higher applied magnetic fields [11], it is found that according to our results, they are more adequate for applications in magnetic refrigeration around room temperature.

Generally, an important index for selecting magnetic material refrigerants is based on the cooling power per unit volume, namely the relative cooling power (RCP) [4], which indicates how much heat can be transferred from the cold end to the hot end of a refrigerator describing a thermodynamic cycle. The first method consist in using not only the

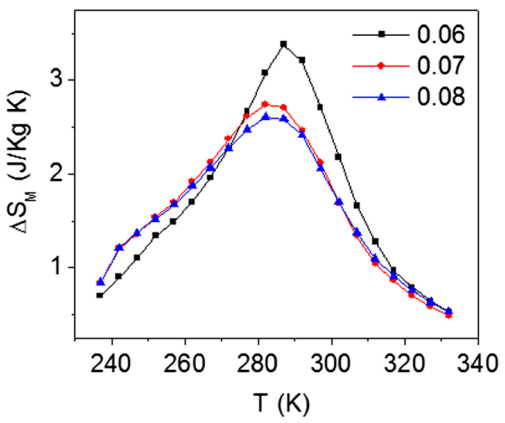

Fig. 5 Variation of magnetic entropy change ΔS_M with temperature of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ manganites under a maximum magnetic field of 3 T. The *error bars* are smaller than data points

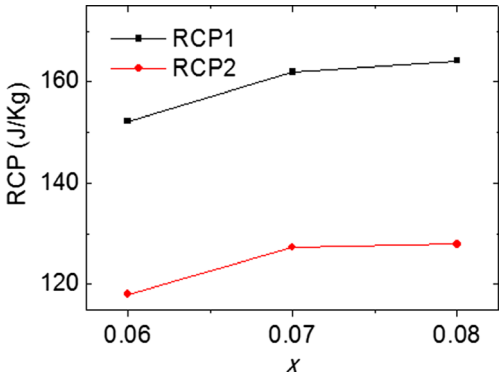

Fig. 6 RCP-1 and RCP-2 of the ceramic $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0.06, 0.07, 0.08$) as a function of x. The *error bars* are smaller than data points

value of magnetocaloric effect (ΔS_M) but also the width of the $\Delta S_M(T)$ curve, which is calculated from the product of the maximum ΔS_M peak value and the full width at half maximum, δT_{FWHM}, RCP-1(S) $= \Delta S_M^{max} \times \delta T_{FWHM}$ [11]. The higher the δT_{FWHM} value, the larger the temperature difference between the hot and the cool ends of the cycle that can be used for operation [12]. This method leads to values of 152 J kg^{-1} for $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$, 162 J kg^{-1} for $La_{0.67}Ca_{0.26}Sr_{0.07}MnO_3$, and 164 J kg^{-1} for $La_{0.67}Ca_{0.25}Sr_{0.08}MnO_3$.

The second RCP-2 values (Fig. 6) were obtained from the area below the $\Delta S_M(T)$ curve using T_{FWHM} as the integration limits, according to

$$RCP - 2 = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T)dT \quad (3)$$

where T_{hot} and T_{cold} are the temperatures of the hot and cold sinks of the refrigerant thermodynamic cycle [13]. This method leads to values of 118 J kg^{-1} for $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$, 127 J kg^{-1} for $La_{0.67}Ca_{0.26}Sr_{0.07}MnO_3$, and 128 J kg^{-1} for $La_{0.67}Ca_{0.25}Sr_{0.08}MnO_3$.

4 Conclusions

In summary, good values of magnetocaloric parameters were observed in $La_{0.67}Ca_{0.27}Sr_{0.06}MnO_3$, $La_{0.67}Ca_{0.26}Sr_{0.07}MnO_3$, and $La_{0.67}Ca_{0.25}Sr_{0.08}MnO_3$ manganese perovskites. The largest value of the RCP is found in $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$, which exhibits good MCE properties. This kind of samples is suitable for their probable use in magnetic refrigeration at room-temperature region.

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